

Graphene-Based Composites for Phosphate Removal

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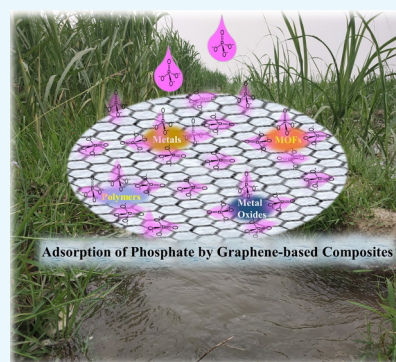


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ABSTRACT: A variety of methods, including chemical precipitation, biological phosphorus elimination, and adsorption, have been described to effectively eliminate phosphorus (P) in the form of phosphate (PO_4^{3-}) from wastewater sources. Adsorption is a simple and easy method. It shows excellent removal performance, cost effectiveness, and the substantial option of adsorbent materials. Therefore, it has been recognized as a practical, environmentally friendly, and reliable treatment method for eliminating P. Nanocomposites have been deployed to remove P from wastewater via adsorption. Nanocomposites offer low-temperature alteration, high specific surface area, adjustable surface chemistry, pore size, many adsorption sites, and rapid intraparticle diffusion distances. In this Mini-Review, we have aimed to summarize the last eight years of progress in P removal using graphene-based composites via adsorption. Ultimately, future perspectives have been presented to boost the progress of this encouraging field.



1. INTRODUCTION

Globally, freshwater for recreation, amusement, farming, and domestic usage is progressively being jeopardized due to the stressors of climate change, growing human demand, and water contamination.¹ Many countries regulate contamination by requiring industries to treat wastewater before dumping it into natural watercourses. However, due to the limited accessibility of high-quality water resources, recycling and repossession of treated wastewater have become imperative to renewable water management. Phosphorus (P) is the primary nutrient pollutant in water bodies such as rivers, streams, lakes, reservoirs, and estuaries.^{1c–e} P often enters water reservoirs via sewage releases, treated wastewater, agricultural and industrial activities, and mining. Excessive concentrations of phosphorus in water bodies can cause eutrophication.² This phenomenon deteriorates water quality due to the overabundant development of plants, e.g., algae. In advanced eutrophication, dissolved oxygen (O_2) can become diminished to threateningly low levels, leading to fish kills.

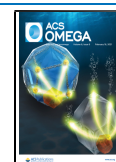
Efficient treatment processes for removing phosphorus are essential to address water quality deterioration.^{3a–c} Conventional procedures such as adsorption, chemical precipitation, biological treatment, and membrane separation have been investigated to eliminate phosphorus.^{3d,e} Among these processes, the adsorption method is currently the most practical phosphorus removal process in water. Phosphorus is found in numerous forms, such as HPO_4^{2-} , H_2PO_4^- , and H_3PO_4 , in ecological environments.⁴ Adsorbed phosphorus can potentially desorb from the adsorbent, and the retrieved phosphate can be further utilized in various applications such as in fertilizers or the production of steel.^{5a} For any adsorption technique, an adsorbent should have a high surface area, pore

volume, and suitable functionalities to sorb contaminants from the soil, water, and air.^{5b} A variety of porous materials such as granular activated carbon, clays, fly ash, zeolites, furnace slag, metal oxides, graphene, graphene oxide, functionalized graphene, metal–organic frameworks, and carbon nanotubes have been studied as adsorbents for phosphorus removal.⁶ Over the past few years, graphene-based composites such as graphene, graphene oxide (GO), reduced graphene oxide (rGO), and modified graphene and graphene oxide have drawn interest for wastewater treatment applications.⁷ Graphene is a 2-D carbon nanomaterial with a single layer of sp^2 -hybridized carbon atoms organized in one plane of six-membered rings. Graphene demonstrates $2630 \text{ m}^2/\text{g}$ of theoretical specific surface area with robust thermal, mechanical, and electrical characteristics.⁸ Functionalized graphene with variable oxygen functionalities is known as graphene oxide (GO). Numerous reviews have been reported on applying graphene-based materials as adsorbents to remove pollutants in water and wastewater treatment.^{8c} However, to the best of our knowledge, no review on phosphate removal in wastewater treatment using graphene-based composites is presented. This review reports the research in graphene-based composites as adsorbents for phosphate removal in water systems.

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2. PHOSPHORUS REMOVAL BY GRAPHENE COMPOSITES

Vasudevan and his research group utilized graphene as an adsorbent to remove phosphate from water ($C_0 = 100$ ppm). Graphene showed an excellent adsorbent capacity of up to 89.37 mg/g at 30 °C.^{9a} They also investigated the effect of pH on phosphate adsorption by varying the solution's pH from 2 to 12. The optimal phosphate adsorption was obtained at a pH of 6–8. Lower adsorption of phosphate was observed in basic conditions (pH > 8) due to the electrostatic repulsion between phosphate ions (PO_4^{2-}) and the negatively charged graphene surface. However, phosphate adsorption is enhanced in acidic media and reaches the peak elimination efficacy of 99.1% at pH 7. Phosphate's adsorption on graphene also intensifies at higher temperatures, indicating the endothermic process. A rise in temperature decreases the interaction between the solvent and solute in the solution. This phenomenon then enhances the interaction between the solute (phosphate) and adsorbent (graphene), ensuring the viability of more active sites for phosphate binding.^{9b} This adsorption method undergoes second-order kinetics, signifying that phosphate's adsorption on graphene is a chemical directing process. GO has also been utilized for the removal of phosphate in wastewater treatment.¹⁰ Similarly, graphene oxide is highly dispersible in water.^{10b} GO has been shown to eliminate 70% of phosphate ($C_0 = 100$ ppm) from water at 30 °C. By incorporating iron nanoparticles on graphene oxide, GO's intake efficiency toward phosphate was increased from 70% to 80%.^{10b}

Recently, Huang and his research group studied the static adsorption of trace concentrations of phosphorus on reduced graphene oxide (rGO).^{10c} Their technology removed 98.9% of P from water. Hydrogen bonds between the reduced graphene oxide and phosphate ions enhanced the adsorption process. To prove the concept, acetaminophen, which also forms hydrogen bonds with rGO, was spiked into the real water as a contender for phosphate adsorption. Consequently, the coexistence of acetaminophen reduced the adsorption of phosphate on rGO.

Overall, graphene, graphene oxide, and reduced graphene have shown an adequate ability to adsorb phosphate. Furthermore, these studies demonstrate the ability of carbonaceous nanomaterials to treat water. However, these materials are ineffective in removing phosphate in the presence of foreign multianions/copollutants due to their nonspecific selectivity toward phosphate. Additionally, these investigations have been performed at the bench scale. Column studies have not yet been conducted in detail.

3. PHOSPHORUS REMOVAL BY FUNCTIONALIZED/MODIFIED GRAPHENE

Graphene and functionalized graphene can be easily dispersed in water homogeneously due to their low density.¹¹ Due to their homogeneous nature, these composites have increased the interaction area with phosphorus.^{11d} Therefore, modified graphene-based composites have been applied widely as adsorbents for phosphate removal. This section will discuss using different types of functionalized and modified graphene-based composites as adsorbents to remove phosphate.

a. Lanthanum/Graphene Composites. Metal cations (M^{n+}) are often recommended as effective constituents to alter the graphene's negatively charged surface to enhance the loading of anions such as PO_4^{2-} and NO_3^- . From the previous studies, it has been established that La^{3+} ions have a high

sorption affinity toward phosphate.¹² Therefore, several investigations have been performed using lanthanum-supported graphene to increase the nanocomposite's adsorption efficiency.^{12b} In one study, lanthanum hydroxide (LaOH) was immobilized onto graphene nanosheets (GNS) via a microwave-mediated hydrothermal process and utilized for phosphate adsorption from an aqueous solution. GNS-LaOH showed two times higher phosphate adsorption capacity (41.96 mg/g) than lanthanum hydroxide supported on activated carbon fiber (15.3 mg/g).^{12c}

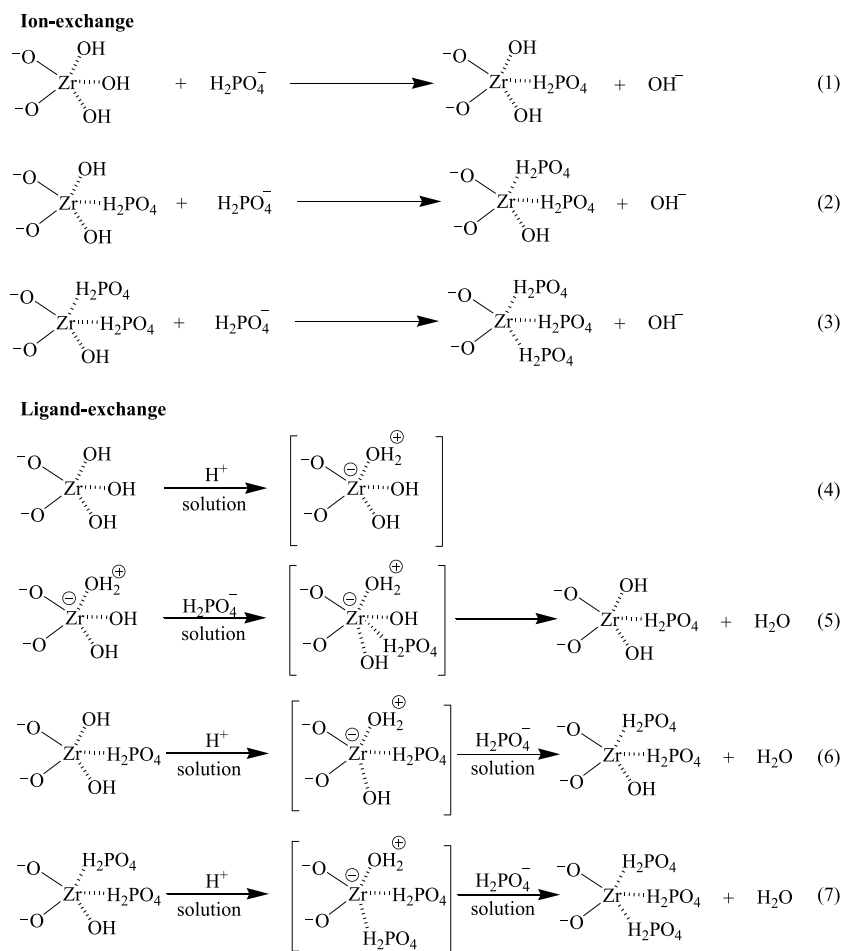
In other studies, 3-D lanthanum oxide immobilized graphene composites exhibited a promising phosphate adsorption capacity of 82.6 mg/g.^{12d} The addition of coexisting anionic species such as SO_4^{2-} , NO_3^- , and Cl^- (8000 ppm) did not affect these adsorbents' efficiency and showed 100% phosphate ($C_0 = 25$ ppm) removal. Similarly, Nouri and his research group developed an innovative technology of lanthanum (La^{3+}) hydrate immobilized magnetic reduced graphene oxide (MG@La) nanocomposites for phosphate removal from river and sewage media. The synthesized MG@La nanocomposite demonstrated a high adsorption capacity of 116.28 mg/g for phosphate.^{13a} The introduction of La^{3+} hydrate on graphene sheets also enhanced their affinity toward oxygen-donor compounds. Also, graphene nanosheets with a high surface as support evade the accumulation of La^{3+} hydroxide nanoparticles. The presence of a high concentration of coexisting ions, including SO_3^{2-} , CO_3^{2-} , Br^- , Cl^- , Fe^{3+} , Cu^{2+} , Ca^{2+} , K^+ , Na^+ , and Zn^{2+} , shows only a minor effect on the adsorption efficiency of MG@La toward phosphate. This may be due to a large number of active sites or the high adsorption capacity of MG@La.

Moreover, MG@La showed excellent chemical stability during the leaching test. Even though the developed adsorbent was shaken for 24 h in water with pH range 4–10, a significantly lower amount of La was released. Recently, innovative phosphate ion-imprinted polymer (GO-IIP) was synthesized by Hu et al. and used for phosphate recovery.^{13b} GO-IIP was fabricated by evolving La(III)-coordinated 3-methylacryloylpropyl bifunctionalized graphene oxide. The developed GO-IIP showed exceptional selectivity and higher adsorption capacity (104.3 mg/g) for phosphate at 25 °C. Also, GO-IIP can be utilized up to seven times, with only about 8.95% loss of initial adsorption capacity. Recently, Li and his research group fabricated a membrane by blending a lanthanum supported metal-organic framework with graphene oxide under pressure and tested for the removal of phosphorus in water. The membrane showed a maximum adsorption capacity at pH = 4. Also, the phosphorus adsorption removal rate can reach 100% when the contaminated water (<100 ppm) is passed through the membrane during the treatment process.^{13c}

Therefore, La-modified graphene-based composites propose a new method for optimizing the highly effective adsorbent for eliminating pollutants from water samples via adsorption.

b. Zirconium/Graphene Composites. Due to their nontoxicity, chemical stability, resistance to oxidation, heterogeneity, and amphoteric nature, zirconium-based oxides have been extensively utilized to eliminate phosphate from water. However, some of these materials have ultrafine characteristics and are very difficult to isolate from water. The fine powders of zirconium-based materials help them to immobilize on appropriate supports to address the leaching

Scheme 1. Plausible Reaction Mechanism of Phosphate Adsorption on the Surface of RGO-Zr in Weakly Acidic Solution



issue.¹⁴ To take advantage of the benefits of both zirconium-based oxides and graphene oxide (GO)/reduced graphene oxide (rGO), the zirconium-loaded reduced graphene oxide (RGO-Zr) adsorbent was synthesized via a one-step green hydrothermal process. These materials were utilized for phosphate adsorption in an aqueous environment under various conditions.^{14b} RGO-Zr showed an adsorption capacity of 27.71 mg P/g at pH 5 and 25 °C. The surface hydroxyl groups may play a key role in phosphate sorption on the adsorbent surface. Phosphate adsorption on the RGO-Zr surface followed the ion exchange and ligand exchange mechanisms in a weakly acidic solution at pH 5 (Scheme 1). Similarly, zirconium-cross-linked graphene oxide/alginate (Zr-GO/Alg) aerogel beads were tested for phosphate uptake performance.^{14c} The integration of graphene oxide provides the composite beads more strength and uniform pores. The Zr-GO/Alg beads showed the highest adsorption capacity of 189.06 mg/g as established by batch and fixed-bed column studies at an optimal pH range of 2.1–4.0. Also, increases in temperature and amount of adsorbent supported enhanced phosphate uptake. The existence of HCO_3^- and F^- repressed phosphate adsorption, whereas the presence of SO_4^{2-} , NO_3^- , and Cl^- did not affect phosphate uptake. By comparing fresh and used Zr-GO/Alg aerogel beads, it was confirmed that the strong binding affinity between phosphate and adsorbents primarily occurred by ligand exchange effect and electrostatic interaction (Scheme 1). Also, spent Zr-GO/Alg aerogel beads

were easily regenerated using 0.1 M NaOH solution, and recycled beads showed high adsorption capacity after five reuses. Recently, Hosseinifard et al. developed a zirconium application, an immobilized nanochitosan–graphene oxide (NCS@GO/H–Zr) adsorbent for the removal of phosphate from water. NCS@GO/H–Zr demonstrated an excellent phosphate uptake of 172.41 mg P/g and retained a 76% phosphate adsorption ability after ten recycles.^{14d}

In summary, zirconium-immobilized graphene-based composites have promising applications in the remediation of water eutrophication. However, further research should be conducted through the column for their scalability and industrial applications.

c. Layered Double Hydroxide/Graphene Composites.

Layered double hydroxides (LDHs) have lamellar hydroxides of divalent (M_I^{2+}) and moderately substituted trivalent (M_{II}^{3+}) cations, which are parted by water molecules and anions in the interlayer spaces to stabilize the overall charge.¹⁵ Due to their capacities to exchange ions, several forms of LDHs have been documented as encouraging and heterogeneous materials for phosphate treatment.¹⁵ However, these processes require prolonged treatment time and insufficient renewal capability. Limited investigations have demonstrated the recycling of used LDHs.^{15c} Extremely concentrated NaCl or NaOH solutions have been utilized to extract the adsorbed phosphate from LDHs. However, this regeneration process is complicated, is

unprofitable for commercial applications, and produces a vast amount of harsh wastewater.¹⁵

Similarly, MgMn-LDH has been employed as a prospective alternative for removing phosphate due to its high stability in solutions, its selectivity for phosphate ions, and the low cost of manganese compounds.¹⁶ By utilizing MgMn-LDH, Tai and his research group established an ultraefficient method of a continuous electrosorption–desorption system for the selective adsorption and discharge of phosphate. They synthesized GO/magnesium manganese-layered double hydroxide (LDH) composites, GO/MgMn-LDH-300, by calcinating at 300 °C.¹⁶ In this process, adsorbed phosphate can be quickly discharged by monitoring the applied voltage. The graphene oxide incorporated within the layered structure enhances the surface area and produces additional mesopores to capture phosphate. Also, oxidation of Mn increases when oxygen-carrying functionalities of GO interact with metal ions. This phenomenon generates different active sites for phosphate adsorption. The synthesized GO/MgMn-LDH-300 demonstrated ultrahigh productivity, selective phosphate elimination, and outstanding recyclability, with phosphate uptake and release rates of 0.97 and 3.56 mg P/g/min, respectively.¹⁶

Recently, the same research group again synthesized a scalable and sustainable hierarchical porous adsorbent using inexpensive *Garcinia subelliptica* leaves as a biodevised natural template for enhanced phosphate adsorption.^{16b} First, MgMn-layered double hydroxide (MgMn-LDH) and GO were grown *in situ* on *Garcinia subelliptica* leaves to get L-GO/MgMn-LDH. Then, L-GO/MgMn-LDH was calcinated at 300 °C to obtain the final hierarchical porous L-GO/MgMn-LDH-300 adsorbent. The leaves are composed of vessels and fibers and possess a natural hierarchical porous structure. Therefore, they can act as a potential biotemplate. The L-GO/MgMn-LDH-300 adsorbent selectively uptakes phosphate and shows high, reusable phosphate adsorption capacity and a desorption rate of 244.08 mg P/g and 85.8%, respectively.^{16b}

Overall, layered double hydroxide/graphene composites are capable, scalable, suitable, and recyclable selective phosphate adsorbents. These techniques propose an appropriate process for efficient and cost-effective phosphate recycling from water.

d. Iron-Based Nanomaterials/Graphene Composites.

In combination with graphene or its derivatives, iron oxide nanomaterials show great potential in catalysis, sensing, water, and wastewater treatment.¹⁷ Previously, an innovative triethylene tetramine-functionalized magnetic graphene oxide chitosan composite (TETA-MGO/CS) with a high uptake efficiency toward phosphate has been synthesized.^{18a} The maximum adsorption capacity of TETA-MGO/CS was found to be 353.36 mg/g at pH 3. The adsorption methods achieved equilibrium in 50 min. Also, adsorbed PO_4^{3-} ions could be released from TETA-MGO/CS and recycled three times. Therefore, TETA-MGO/CS has been investigated as an efficient and renewable adsorbent in phosphate removal.

Losic and his research group developed a technology of 3-D graphene aerogels fabricated with goethite ($\alpha\text{-FeOOH}$) and magnetite (Fe_3O_4) nanoparticles for capturing phosphates in water.^{18b} These synthesized aerogels demonstrated a high capacity to eliminate phosphate ($C_0 = 200$ ppm) up to 350 mg/g. Similarly, $\alpha\text{-Fe}_2\text{O}_3$ -immobilized graphene oxide (GO- Fe_2O_3) was utilized for the adsorption of phosphate.^{18c} GO- Fe_2O_3 adsorbed 93.28 mg/g phosphate ($C_0 = 50$ ppm) at pH 6.0 and 25 °C. The synthesized GO- Fe_2O_3 showed very stable phosphate adsorption capacity between the pH range of 2.0–

10.5 and the temperature range of 20–60 °C. GO- Fe_2O_3 achieved adsorption equilibrium within 5 min. Mainly, GO- Fe_2O_3 follows the electrostatic attraction (physical adsorption) and ion exchange (chemical adsorption) mechanisms to remove the phosphate in treatment application. In another study, akaganeite nanorods ($\beta\text{-FeOOH}$) integrated on GO sheets were utilized to remove phosphate from water at pH 7 and 30 °C.^{18d} The incorporation of GO during the preparation of $\beta\text{-FeOOH}$ nanorods raises the characteristic ratio of rods from 5 to 7. The kinetics data demonstrated second-order kinetics, and the equilibrium condition was attained within 2 h. The removal of phosphate was enhanced at a lower pH and decreased at a higher pH solution. $\beta\text{-FeOOH/GO}$ displayed good recyclability at different pH solutions and showed a maximum of 78% at pH 7 and 30 °C.

Overall, iron-based nanomaterials/graphene composites are stable, recyclable, and scalable adsorbents to remove phosphate in wastewater treatment applications. Therefore, these materials can be an excellent choice to deal with phosphate-contaminated water for commercial purposes.

e. Other Miscellaneous Graphene-Based Composites.

Graphene-based composites possess high chemical stability and good mechanical strength.¹⁹ Titania-functionalized graphene oxide (TiO_2/GO) has been widely utilized in water treatment applications compared to other oxidative derivatives.^{19c} The large surface area of graphene oxide and its high uptake efficiency also boost titanium/graphene-based composites' adsorption capacity. Sakulpaian and his research group synthesized titania-functionalized graphene oxide by the sol-gel method. TiO_2/GO composites yielded better adsorption results than titania and graphene oxide.^{20a} The synthesized TiO_2/GO showed 30.4 mg/g of phosphate adsorption capacity at pH 6. Phosphate adsorption decreases at high pH levels due to a rise in the repulsion between phosphate anions and the oxygen-carrying functional group of adsorbent surfaces. Similarly, Martinez and his research group performed a comparative study between GO and GO-functionalized silver nanoparticles (GO@AgNPs) as adsorbents to eliminate phosphate from water samples. An amount of 20 mg of GO removed 75% phosphate ($C_0 = 30$ ppm) at pH 10. Only 500 μL of GO@AgNPs eliminated 100% phosphate ($C_0 = 30$ ppm) at pH 7.^{20b} Recently, Keggin-type aluminum polyoxocation species, Al30, modified graphene oxide nanosheets, and triaminotriazine-functionalized GO composites were investigated for the efficient removal of phosphate.^{20c} These adsorbents are cost-effective and can be reused up to several cycles without significant loss of their uptake efficiency. Further, these heterogeneous composites could be synthesized at a large scale for commercial use in the industrial application of wastewater treatment.

f. Conclusions and Future Perspectives. Graphene is increasingly appealing to more researchers and scientists due to its exceptional thermal, electronic, and mechanical characteristics. Modified graphene-based materials have been synthesized by cross-linking organic scaffolds via noncovalent and covalent interaction and impregnating inorganic metals. These modified/functionalized graphene-based composites demonstrate exceptional and enhanced abilities in numerous fields. In this mini-review, we summarize the applications of graphene and functionalized graphene-based composites in removing phosphorus in the form of phosphate. The elimination of phosphorus from contaminated water is a worldwide concern as an excess of phosphorus instigates negative ecological

effects. Excess phosphorus can cause eutrophication, which further leads to inferior water quality and marine life damage. Many treatment processes have been investigated to eliminate phosphorus from water to stop the excess toxic ecological effects from phosphorus. Among many techniques, the adsorption method has its exclusive benefits for practical and large-scale applications, such as high efficiency and easy operation.

The present mini-review focuses on phosphate removal in wastewater treatment using graphene-based composites. Several metals (e.g., titania, zirconium, iron, layered double hydroxide, lanthanum, aluminum, and silver) and modified graphene composites have been studied for the effective adsorption of phosphate. Among these, iron-based nanomaterials/graphene composites and layered double hydroxide/graphene composites have shown promising, stable, recyclable, and scalable adsorbents for the selective removal of phosphate. Some biomasses (e.g., cellulose and chitosan) and functionalized graphene-based composites have also been investigated for the cost-effective removal of phosphate from water.

These graphene-based adsorbents can be an excellent alternative to treat phosphate. However, most of the studies have been performed at the bench scale. Further research needs to be conducted at the pilot scale, including column study for their industrialization. This will most likely be done by further examining phosphorus elimination mechanisms and favorable removal conditions on a large scale during column studies.

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Notes

The authors declare no competing financial interest.

Biographies



Dr. Mallikarjuna N. Nadagouda received his Ph.D. from India in 2003. While earning his Ph.D., Dr. Nadagouda worked with professor

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REFERENCES

- (1) (a) Ramasahayam, S. K.; Guzman, L.; Gunawan, G.; Viswanathan, T. A Comprehensive Review of Phosphorus Removal Technologies and Processes. *J. Macromol. Sci., Part A: Pure Appl. Chem.* **2014**, *51*, 538–545. (b) Bunce, J. T.; Ndam, E.; Ofiteru, I. D.; Moore, A.; Graham, D. W. A Review of Phosphorus Removal Technologies and Their Applicability to Small-scale Domestic Wastewater Treatment Systems. *Front. Environ. Sci.* **2018**, *6*, 8. (c) Martin, E.; Lalley, J.; Wang, W.; Nadagouda, M. N.; Sahle-Demessie, E.; Chae, S. Phosphate Recovery from Water Using Cellulose Enhanced Magnesium Carbonate Pellets: Kinetics, Isotherms, and Desorption. *Chem. Eng. J.* **2018**, *352*, 612–624. (d) Ren, X.; Tan, X.; Hayat, T.; Alsaedi, A.; Wang, X. Co-sequestration of Zn(II) and Phosphate by Gamma-Al₂O₃: from Macroscopic to Microscopic Investigation. *J. Hazard. Mater.* **2015**, *297*, 134–145. (e) Han, C.; Lalley, J.; Iyanna, N.; Nadagouda, M. N. Removal of Phosphate Using Calcium and Magnesium-modified Iron-Based Adsorbents. *Mater. Chem. Phys.* **2017**, *198*, 115–124. (f) Boholm, Å; Prutzer, M. Experts' Understandings of Drinking Water Risk Management in a Climate Change Scenario. *Clim. Risk Manag.* **2017**, *16*, 133–144. (g) Misra, A. K. Climate Change and Challenges of Water and Food Security. *Int. J. Sustainable Built Environ.* **2014**, *3*, 153–165. (h) Maiolo, M.; Mendicino, G.; Pantusa, D.; Senatore, A. Optimization of Drinking Water Distribution Systems in Relation to the Effects of Climate Change. *Water* **2017**, *9*, 803.
- (2) (a) Odoemena, K. I.; MD Rowshon, K.; Hasfalina Binti, C. M. Advances in Utilization of Wastewater in Agricultural Practice: A Technical Note. *Irrig. Drain.* **2020**, *69*, 149–163. (b) Silva, M.; Murzin, V.; Zhang, L.; Baltrus, J.; Baltrusaitis, J. Transition Metal Doped MgO Nanoparticles for Nutrient Recycling: An Alternate Mg Source for Struvite Synthesis from Wastewater. *Environ. Sci.: Nano* **2020**, *7*, 3482–3496.
- (3) (a) Hermassi, M.; Valderrama, C.; Dosta, J.; Cortina, J. L.; Batis, N. H. Evaluation of Hydroxyapatite Crystallization in a Batch Reactor for the Valorization of Alkaline Phosphate Concentrates from Wastewater Treatment Plants Using Calcium Chloride. *Chem. Eng. J.* **2015**, *267*, 142–152. (b) Lalley, J.; Han, C.; Li, X.; Dionysiou, D. D.; Nadagouda, M. N. Phosphate Adsorption Using Modified Iron Oxide-Based Sorbents in Lake Water: Kinetics, Equilibrium, and Column Tests. *Chem. Eng. J.* **2016**, *284*, 1386–1396. (c) Li, F. H.; Wu, W. H.; Li, R. Y.; Fu, X. R. Adsorption of Phosphate by Acid-modified Fly Ash and Palygorskite in Aqueous Solution: Experimental and Modeling. *Appl. Clay Sci.* **2016**, *132*, 343–352. (d) Lalley, J.; Han, C.; Mohan, G. R.; Dionysiou, D. D.; Speth, T. F.; Garland, J.; Nadagouda, M. N. Phosphate Removal Using Modified Bayoxide®E33 Adsorption Media. *Environ. Sci. Water Res. Technol.* **2015**, *1*, 96–107. (e) Vanotti, M. B.; Garcia-González, M. C.; Molinuevo-Salces, B.; Riaño, B. *Ed.ial: New Processes for Nutrient Recovery from Wastes*; Frontiers Media SA, 2019.
- (4) (a) Batstone, D. J.; Hülsen, T.; Mehta, C. M.; Keller, J. Platforms for Energy and Nutrient Recovery from Domestic Wastewater: A Review. *Chemosphere* **2015**, *140*, 2–11. (b) Macura, B.; Johannesdottir, S. L.; Piniewski, M.; Haddaway, N. R.; Kvarnström, E. Effectiveness of Ecotechnologies for Recovery of Nitrogen and Phosphorus from Anaerobic Digestate and Effectiveness of the Recovery Products as Fertilisers: A Systematic Review Protocol. *Environmental Evidence* **2019**, *8*, 29.
- (5) (a) Perera, M. K.; Englehardt, J. D.; Dvorak, A. C. Technologies for Recovering Nutrients from Wastewater: A Critical Review. *Environ. Eng. Sci.* **2019**, *36*, 511–529. (b) Sophia, C.; Lima, E. C. Removal of Emerging Contaminants from the Environment by Adsorption. *Ecotoxicol. Environ. Saf.* **2018**, *150*, 1–17.
- (6) (a) Nakarmi, A.; Bourdo, S. E.; Ruhl, L.; Kanel, S.; Nadagouda, M.; Alla, P. K.; Pavel, I.; Viswanathan, T. Benign Zinc Oxide Betaine-modified Biochar Nanocomposites for Phosphate Removal from Aqueous Solutions. *J. Environ. Manage.* **2020**, *272*, 111048. (b) Nadagouda, M. N., Water Warriors Inc, Adsorbates Structures for the Removal of Phosphate and Ammonia from Wastewater and Methods of Use. U.S. Patent Application 17151979, 2021. (c) Wang, J.; Xia, Y. Fe-Substituted Isoreticular Metal-Organic Framework for Efficient and Rapid Removal of Phosphate. *ACS Appl. Nano Mater.* **2019**, *2*, 6492–6502. (d) Mazloomi, S.; Yousefi, M.; Nourmoradi, H.; Shams, M. Evaluation of Phosphate Removal from Aqueous Solution using Metal Organic Framework; Isotherm, Kinetic and Thermodynamic Study. *J. Environ. Health Sci. Eng.* **2019**, *17*, 209–218.
- (7) (a) Wang, S.; Sun, H.; Ang, H. M.; Tadó, M. O. Adsorptive Remediation of Environmental Pollutants Using Novel Graphene-based Nanomaterials. *Chem. Eng. J.* **2013**, *226*, 336–347. (b) Ren, X.; Wu, Q.; Xu, H.; Shao, D.; Tan, X.; Shi, W.; Chen, C.; Li, J.; Chai, Z.; Hayat, T.; Wang, X. New Insight into GO, Cadmium (II), Phosphate Interaction and its Role in GO Colloidal Behavior. *Environ. Sci. Technol.* **2016**, *50*, 9361–9369. (c) Wang, W.; Xu, Z.; Zhang, X.; Wimmer, A.; Shi, E.; Qin, Y.; Zhao, X.; Zhou, B.; Li, L. Rapid and Efficient Removal of Organic Micropollutants from Environmental Water using a Magnetic Nanoparticles-attached Fluorographene-based Sorbent. *Chem. Eng. J.* **2018**, *343*, 61–68. (d) Tabish, T. A.; Memon, F. A.; Gomez, D. E.; Horsell, D. W.; Zhang, S. A Facile Synthesis of Porous Graphene for Efficient Water and Wastewater Treatment. *Sci. Rep.* **2018**, *8*, 1–14. (e) Sabzevari, M.; Cree, D. E.; Wilson, L. D. Graphene Oxide-Chitosan Composite Material for Treatment of a Model Dye Effluent. *ACS omega* **2018**, *3*, 13045–13054. (f) Thakur, K.; Kandasubramanian, B. Graphene and Graphene Oxide-based Composites for Removal of Organic Pollutants: A Review. *J. Chem. Eng. Data* **2019**, *64*, 833–867.
- (8) (a) Alam, S. N.; Sharma, N.; Kumar, L. Synthesis of Graphene Oxide (GO) by Modified Hummers Method and its Thermal Reduction to Obtain Reduced Graphene Oxide (rGO). *Graphene* **2017**, *6*, 1–18. (b) Zhu, Y.; Murali, S.; Cai, W.; Li, X.; Suk, J. W.; Potts, J. R.; Ruoff, R. S. Graphene and Graphene Oxide: Synthesis, Properties, and Applications. *Adv. Mater.* **2010**, *22*, 3906–3924. (c) Gulati, A.; Kakkar, R. Graphene-based Adsorbents for Water Remediation by Removal of Organic Pollutants: Theoretical and Experimental Insights. *Chem. Eng. Res. Des.* **2020**, *153*, 21–36.
- (9) (a) Vasudevan, S.; Lakshmi, J. The Adsorption of Phosphate by Graphene from Aqueous Solution. *RSC Adv.* **2012**, *2*, 5234–5242. (b) Kumar, P. S.; Yaashikaa, P. R.; Ramalingam, S. Efficient Removal of Nitrate and Phosphate Using Graphene Nanocomposites. In *A New Generation Material Graphene: Applications in Water Technology*; Naushad, M., Ed.; Springer: Cham, 2019; pp 287–307.
- (10) (a) Jun, T. S.; Park, N. H.; So, D. S.; Lee, J. W.; Shim, K. B.; Ham, H. Phosphate Removing by Graphene Oxide in Aqueous Solution. *J. Korean Cryst. Growth Cryst. Technol.* **2013**, *23*, 325–328. (b) Ren, X.; Wu, Q.; Xu, H.; Shao, D.; Tan, X.; Shi, W.; Chen, C.; Li, J.; Chai, Z.; Hayat, T.; Wang, X. New Insight into GO, Cadmium (II), Phosphate Interaction and its Role in GO Colloidal Behavior. *Environ. Sci. Technol.* **2016**, *50*, 9361–9369. (c) Wang, Y.; Yang, Q.; Huang, H. Effective Adsorption of Trace Phosphate and Aluminum in Realistic Water by Carbon Nanotubes and Reduced Graphene Oxides. *Sci. Total Environ.* **2019**, *662*, 1003–1011.
- (11) (a) Du, J.; Cheng, H. M. The Fabrication, Properties, and Uses of Graphene/Polymer Composites. *Macromol. Chem. Phys.* **2012**, *213*, 1060–1077. (b) Verma, S.; Mungse, H. P.; Kumar, N.; Choudhary, S.; Jain, S. L.; Sain, B.; Khatri, O. P. Graphene Oxide: An Efficient and Reusable Carbocatalyst for Aza-Michael Addition of Amines to Activated Alkenes. *Chem. Commun.* **2011**, *47*, 12673–12675. (c) Mungse, H. P.; Verma, S.; Kumar, N.; Sain, B.; Khatri, O. P. Grafting of Oxo-vanadium Schiff base on Graphene Nanosheets and its Catalytic Activity for the Oxidation of Alcohols. *J. Mater. Chem.* **2012**, *22*, 5427–5433. (d) Xu, L.; Wang, J. The Application of Graphene-based Materials for the Removal of Heavy Metals and Radionuclides from Water and Wastewater. *Crit. Rev. Environ. Sci. Technol.* **2017**, *47*, 1042–1105.
- (12) (a) He, H.; Li, C.; Tian, Y.; Wu, P.; Hou, X. Phosphorescent Differential Sensing of Physiological Phosphates with Lanthanide ions-modified Mn-doped ZnCdS Quantum Dots. *Anal. Chem.* **2016**, *88*, 5892–5897. (b) Zhang, L.; Wang, Z.; Xu, X.; Chen, C.; Gao, B.; Xiao, X. Insights into the Phosphate Adsorption Behavior onto 3D Self-assembled Cellulose/Graphene Hybrid Nanomaterials Embed-

ded with Bimetallic Hydroxides. *Sci. Total Environ.* **2019**, *653*, 897–907. (c) Zhang, L.; Zhou, Q.; Liu, J.; Chang, N.; Wan, L.; Chen, J. Phosphate Adsorption on Lanthanum Hydroxide-Doped Activated Carbon Fiber. *Chem. Eng. J.* **2012**, *185*, 160–167. (d) Chen, M.; Huo, C.; Li, Y.; Wang, J. Selective Adsorption and Efficient Removal of Phosphate from Aqueous Medium with Graphene-Lanthanum Composite. *ACS Sustainable Chem. Eng.* **2016**, *4*, 1296–1302.

(13) (a) Nodeh, H. R.; Sereshti, H.; Afsharian, E. Z.; Nouri, N. Enhanced Removal of Phosphate and Nitrate Ions from Aqueous Media Using Nanosized Lanthanum Hydrous Doped on Magnetic Graphene Nanocomposite. *J. Environ. Manage.* **2017**, *197*, 265–274. (b) Liu, Z.; Wu, W.; Liu, Y.; Hu, X. Preparation of Surface Anion Imprinted Polymer by Developing a La (III)-coordinated 3-methacryloxyethyl-propyl Bi-functionalized Graphene Oxide for Phosphate Removal. *J. Taiwan Inst. Chem. Eng.* **2018**, *85*, 282–290. (c) Wei, N.; Zheng, X.; Li, Q.; Gong, C.; Ou, H.; Li, Z. Construction of lanthanum modified MOFs graphene oxide composite membrane for high selective phosphorus recovery and water purification. *J. Colloid Interface Sci.* **2020**, *565*, 337–344.

(14) (a) Pourbeyram, S.; Soltanpour, M.; Fathalipour, S. Determination of Phosphate in Human Serum with Zirconium/Reduced Graphene Oxide Modified Electrode. *Anal. Sci.* **2019**, *35*, 739–743. (b) Luo, X.; Wang, X.; Bao, S.; Liu, X.; Zhang, W.; Fang, T. Adsorption of Phosphate in Water Using One-step Synthesized Zirconium-Loaded Reduced Graphene Oxide. *Sci. Rep.* **2016**, *6*, 39108. (c) Shan, S.; Tang, H.; Zhao, Y.; Wang, W.; Cui, F. Highly Porous Zirconium-crosslinked Graphene Oxide/Alginate Aerogel Beads for Enhanced Phosphate Removal. *Chem. Eng. J.* **2019**, *359*, 779–789. (d) Salehi, S.; Hosseini, M. Optimized Removal of Phosphate and Nitrate from Aqueous Media Using Zirconium Functionalized Nanochitosan-Graphene Oxide Composite. *Cellulose* **2020**, *27*, 8859.

(15) (a) Hong, S. P.; Yoon, H.; Lee, J.; Kim, C.; Kim, S.; Lee, J.; Lee, C.; Yoon, J. Selective Phosphate Removal Using Layered Double Hydroxide/Reduced Graphene Oxide (LDH/rGO) Composite Electrode in Capacitive Deionization. *J. Colloid Interface Sci.* **2020**, *564*, 1–7. (b) Huang, W.; Zhang, Y.; Li, D. Adsorptive Removal of Phosphate from Water Using Mesoporous Materials: A Review. *J. Environ. Manage.* **2017**, *193*, 470–482. (c) Prasad, C.; Tang, H.; Liu, W. Magnetic Fe₃O₄ Based Layered Double Hydroxides (LDHs) Nanocomposites (Fe₃O₄/LDHs): Recent Review of Progress in Synthesis, Properties and Applications. *J. Nanostructure Chem.* **2018**, *8*, 393–412. (d) Das, J.; Patra, B. S.; Baliarsingh, N.; Parida, K. M. Adsorption of Phosphate by Layered Double Hydroxides in Aqueous Solutions. *Appl. Clay Sci.* **2006**, *32*, 252–260.

(16) (a) Lai, Y. T.; Liu, W. T.; Chen, L. J.; Chang, M. C.; Lee, C. Y.; Tai, N. H. Electro-assisted Selective Uptake/release of Phosphate Using a Graphene Oxide/MgMn-layered Double Hydroxide Composite. *J. Mater. Chem. A* **2019**, *7*, 3962–3970. (b) Lai, Y. T.; Huang, Y. S.; Chen, C. H.; Lin, Y. C.; Jeng, H. T.; Chang, M. C.; Chen, L. J.; Lee, C. Y.; Hsu, P. C.; Tai, N. H. Green Treatment of Phosphate from Wastewater Using a Porous Bio-Templated Graphene Oxide/MgMn-Layered Double Hydroxide Composite. *iScience* **2020**, *23*, 101065.

(17) (a) Akram, M. Y.; Ahmed, S.; Li, L.; Akhtar, N.; Ali, S.; Muhyodin, G.; Zhu, X. Q.; Nie, J. N-doped Reduced Graphene Oxide Decorated with Fe₃O₄ Composite: Stable and Magnetically Separable Adsorbent Solution for High Performance Phosphate Removal. *J. Environ. Chem. Eng.* **2019**, *7*, 103137. (b) Sereshti, H.; Zamiri Afsharian, E.; Esmaili Bidhendi, M.; Rashidi Nodeh, H.; Afzal Kamboh, M.; Yilmaz, M. Removal of Phosphate and Nitrate Ions Aqueous Using Strontium Magnetic Graphene Oxide Nanocomposite: Isotherms, Kinetics, and Thermodynamics Studies. *Environ. Prog. Sustainable Energy* **2020**, *39*, 13332.

(18) (a) Wang, H.; Zhang, P.; Liu, J. Triethylene Tetramine Functionalized Magnetic Graphene Oxide Chitosan Composite with Superior Capacity for the Removal of Phosphate. *J. Chem. Eng. Data* **2017**, *62*, 3341–3352. (b) Tran, D. N.; Kabiri, S.; Wang, L.; Losic, D. Engineered Graphene-nanoparticle Aerogel Composites for Efficient

Removal of Phosphate from Water. *J. Mater. Chem. A* **2015**, *3*, 6844–6852. (c) Bai, L.; Yuan, L.; Ji, Y.; Yan, H. Effective Removal of Phosphate from Aqueous by Graphene Oxide Decorated with α -Fe₂O₃: Kinetic, Isotherm, Thermodynamic and Mechanism Study. *Arabian J. Sci. Eng.* **2018**, *43*, 3611–3620. (d) Harijan, D. K.; Chandra, V. Akaganeite Nanorods Decorated Graphene Oxide Sheets for Removal and Recovery of Aqueous Phosphate. *J. Water Process Eng.* **2017**, *19*, 120–125.

(19) (a) Papageorgiou, D. G.; Kinloch, I. A.; Young, R. J. Mechanical Properties of Graphene and Graphene-based Nanocomposites. *Prog. Mater. Sci.* **2017**, *90*, 75–127. (b) Aswin Kumar, I.; Naushad, M.; Viswanathan, N. Microfabrication of Triazine Functionalized Graphene Oxide Anchored Alginate Bead System for Effective Nutrients Removal. *J. Chem. Eng. Data* **2020**, *65*, 2712–2724. (c) Li, C.; Sun, W.; Lu, Z.; Ao, X.; Yang, C.; Li, S. Systematic Evaluation of TiO₂-GO-modified Ceramic Membranes for Water Treatment: Retention Properties and Fouling Mechanisms. *Chem. Eng. J.* **2019**, *378*, 122138.

(20) (a) Sakulpaisan, S.; Vongsetskul, T.; Reamouppaturm, S.; Luangkachao, J.; Tantirungrotechai, J.; Tangboriboonrat, P. Titania-functionalized Graphene Oxide for an Efficient Adsorptive Removal of Phosphate Ions. *J. Environ. Manage.* **2016**, *167*, 99–104. (b) Vicente-Martínez, Y.; Caravaca, M.; Soto-Meca, A.; De Francisco-Ortiz, O.; Gimeno, F. Graphene Oxide and Graphene Oxide Functionalized with Silver Nanoparticles as Adsorbents of Phosphates in Waters. A Comparative Study. *Sci. Total Environ.* **2020**, *709*, 136111. (c) Tahmasebi, E. Insights into the Adsorption Mechanism of Al₃₀ Polyoxocations-modified Graphene Oxide Nanosheets for Efficient Removal of Phosphate, Chromate and Selenate Oxyanions: A Comparative Study. *J. Mol. Liq.* **2020**, *299*, 112111.